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# Investigation of Inclusions in Armco Ingot Iron

Edwin J. Duncan

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INVESTIGATION OF INCLUSIONS IN  
ARMCO INGOT IRON

A thesis submitted to the Department  
of Metallurgy in partial fulfilment of the  
requirements for the degree of Bachelor of  
Science in Metallurgical Engineering.

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Edwin J. Duncan

Montana School of Mines

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## ABSTRACT

Various chemical and electrolytic separation methods were investigated in an attempt to separate the inclusions in Armco ingot iron. Residues obtained were X-rayed for identification purposes. The microstructures of this iron were studied with the object of determining the relative sizes, locations, and possible compositions of the inclusions. The inclusions form both at the grain boundaries, where they are relatively the same size, and within the grains, where there is a large size distribution. The single-phase structure of the inclusions is apparently magnetite ( $\text{Fe}_3\text{O}_4$ ).



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## INTRODUCTION

The fact that the nature, type, and composition of inclusions found in iron and steel is becoming increasingly important is well borne out by the amount of research that has been and is presently being carried out by the major iron and steel companies of this country. Because variations in inclusions may be causing variations in the physical and magnetic properties of Armco iron, research on the separation and identification of these inclusions is presently progressing more rapidly than at any time during the past.

Both producer and user are interested not only in the type but also in the size and distribution of the inclusions and in their total quantity. This is done in one of two ways. The first of these, the inclusion count procedure, uses methods based on an actual count of inclusions present in a definite area on a photomicrograph of the sample and compares this with a standard set of photomicrographs having known types of inclusions. The second approach to this problem is the extraction of nonmetallic matter from the iron by dissolving the metal, whereby a residue is obtained which may then be analyzed for chemical content.<sup>1</sup>

Several methods have been advanced for inclusion separation from ingot iron. These are all based on previous work done on other types of steel.<sup>2</sup>



In general, methods of separation may be divided into two classifications; namely, chemical and electrolytic. Both methods rely upon chemical attack of the iron without chemical attack of the inclusions. In the former various chemicals are used to dissolve the iron, leaving the inclusions to be collected for analysis. The latter uses the iron as an anode with various cathodes and electrolytes. The inclusions are collected in extraction thimbles for more research.<sup>3</sup>

Many difficulties arise in the separation of inclusions from steels. Contamination of the residues with insoluble materials such as carbides and hydrolyzed iron salts may occur, giving false results. The lack of reproducibility of results in any one method is also a possibility.<sup>4</sup> Recovery of the inclusions following decomposition of a representative sample is also a difficulty to be looked for at the outset of any investigation of this type.



## THEORY

Inclusions have been defined in a number of different ways. They have been termed "substances mechanically entangled by a fused alloy"<sup>5</sup> and as "extraneous bodies held in a metallic mass which remained too short a time in a sufficiently fluid state to allow such inclusions to separate from the mass by reason of difference of density."<sup>6</sup> Inclusions are impurities, for example, elements or compounds, which are not intended or desired in the metal. For this reason the most comprehensive and precise definition of inclusions is "inclusions are impurities mechanically associated with the metal at ordinary temperatures."<sup>7</sup>

Inclusions may be found in iron and steel as a result of two processes: those which are entrapped in the iron or steel inadvertently, and those which are separated from it because of a change in temperature or composition. The first type originates from particles of nonmetallic matter that are occluded in the iron when it is in the molten state. The second type is produced either in the molten or the solid state as the result of separation of oxide, sulphide, nitride, or other nonmetallic compounds from the iron or steel. Because the latter type of inclusions are the results of reactions within the iron itself, it is impossible to completely control the inclusions which form. The best that can be done is to control the kind and amount of inclusions within such limits that the steel is free



from injurious or detrimental effects, or to insure the desired inclusions are present.<sup>8</sup>

For the most part, inclusions are oxides, sulphides, and nitrides, or various combinations of these. It is customary to eliminate carbides from the category of inclusions. This is because the amount and distribution of carbides largely determines the properties of a steel, while inclusions generally exert small if any effect on the properties.

The types of inclusions that originate as a result of reactions taking place in the body of the molten or solidifying metal do so by one of five methods. The inclusions may be caused by the following:

1. Oxidation such as may occur during refining or tapping.
2. Deoxidation by added alloys.
3. Change in equilibrium constants as the steel cools.
4. Decreased solubility with lower temperature.
5. Change in concentration owing to segregation during freezing.<sup>9</sup>

The materials which compose inclusions are chemical compounds or mixtures of compounds.<sup>10</sup> In most steels that have been investigated, inclusions have consisted of the lower oxides, nitrides, and sulphides. This is a direct result of the steel following the laws of heterogeneous equilibrium. As the steel is cooling, new sets of equi-



librium conditions are being approached continuously.

These changes in equilibrium conditions are brought about by variations in temperature and composition.

"When equilibrium has been maintained between an inclusion and the steel, the phase or phases in the inclusion will be those which can exist in the presence of the metal phase represented by the steel."<sup>11</sup> This is the main reason for the observance of the lower valence states in the inclusions.

The possibility of finding inclusions resulting from the occlusion of foreign particles is very slight in ingot iron because of the extreme care utilized in the production. High grade refractories and high purity raw materials also work against this possibility.<sup>12</sup> In addition, large specific gravity differences promote the separation of nonmetallics from molten iron.

There are several methods proposed for studying non-metallic inclusions. The first test, or inspection test, for inclusions is made with the aid of a metallographic microscope. Here such inclusions are exposed on a surface and are subjected to various visual and etching tests. This method may or may not be reliable depending upon sampling techniques. This is a rapid method and has the advantage of showing the location of the inclusions, which could frequently be more important than the type or amount.

Suitable chemical treatment has also been advanced for the separation of the inclusions from the parent to



determine their chemical composition and quantity.

X-ray techniques may supplement this latter method of analysis to determine actual phases or combinations present.<sup>13</sup>



## OUTLINE OF EXPERIMENTATION

The experimentation planned and followed with the final result to be separation and identification of the nonmetallic inclusions in Armco iron was:

- (A.) To evaluate a series of extraction methods to determine which method would provide the cleanest separation of the oxides present, and
- (B.) To study the microstructures of ingot iron samples with the object of determining the relative sizes, locations, and possible compositions of the inclusions.

In more detail the procedure was as follows:

1. Mount, polish, and photograph a sample of the iron to obtain an inclusion count by lineal analysis. From the results of this step, location of inclusions could also be noted, and a proper sample size for inclusion extraction could be calculated.
2. Select a series of electrolytic and chemical methods which appear to have promise.
3. Separate the inclusions using selected chemical and electrolytic methods.
4. X-ray the inclusions for identification.



## SAMPLING

All samples for this investigation were obtained through the courtesy of Mr. Arthur P. Woods, Jr. of the American Rolling Mills Company Research Laboratory of Middletown, Ohio. The samples were cut from the edge of a hot rolled coil. The samples were taken next to the coil edge to provide uniform analysis. The coil cross section analysis was:

C	-	0.0130%
Mn	-	0.0290%
P	-	0.0020%
S	-	0.0160%
Si	-	0.0020%
Cu	-	0.1300%
N	-	0.0022%



## EXPERIMENTAL PROCEDURE

### A. Lineal Analysis.

To determine an approximate sample size for investigation, it was necessary to perform some type of metallographic analysis. A specimen was cut from the sample, mounted, ground and polished. A photomicrograph

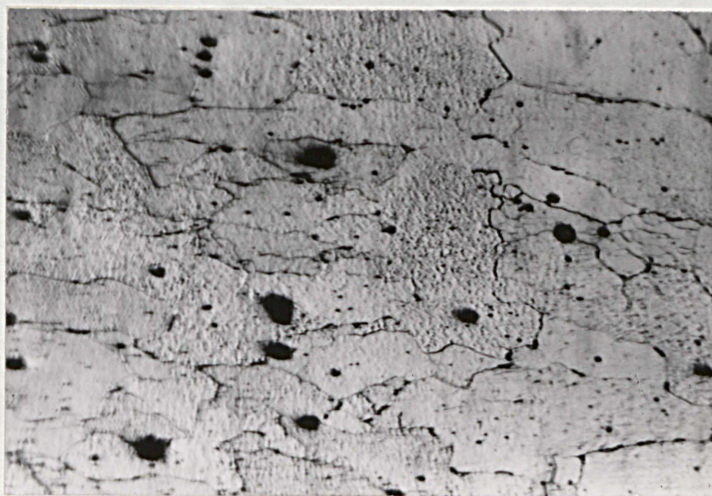


Fig. 1

PHOTOMICROGRAPH OF ARMCO INGOT IRON

4% Nital Etch - 15 sec. 400x

(Fig. 1) was taken and subsequently enlarged to 1200x to increase the accuracy of measurement. Lineal analysis was performed as follows: lines, both horizontal and vertical, were placed on this enlargement at  $\frac{1}{4}$  in. intervals, and measurements were taken on these lines.



The following calculations are based on these measurements.

Total length of lines measured - 243.60 cm.

Total length of line overlapping  
inclusions - 18.40 cm.

$$\frac{18.40}{243.60} \times 100 = 7.55\% \text{ Volume per cent of inclusions.}$$

For weight determination the inclusion density was assumed to approximate the density of  $\text{Fe}_3\text{O}_4$  (5.18 g/cc). The density of iron is 7.89 g/cc. Assuming inclusions to be completely  $\text{Fe}_3\text{O}_4$  a sample size was calculated.

For 100 cc. Fe plus  $\text{Fe}_3\text{O}_4$

$$7.55 \text{ cc. } \text{Fe}_3\text{O}_4 \times 5.18 = 39 \text{ gr.}$$

$$92.45 \text{ cc. Fe} \times 7.89 = \underline{728 \text{ gr.}}$$

767 gr. Total

$$\frac{767}{39} = \frac{x}{1}$$

$x = 18.7$  gr. of Fe sample required for a one gram sample of inclusions. A one gram sample was deemed sufficient for the X-ray diffraction analysis.



## B. Extractive Methods.

On the basis of calculations made from lineal analysis, samples weighing approximately 20 grams were cut with a hacksaw from the Armco sheet. It was thought advisable to use solid samples to avoid mechanical loss of inclusions during sampling operations. The average sample measured approximately  $\frac{1}{4}$  cm x  $2\frac{1}{2}$  cm x  $6\frac{1}{2}$  cm.

Following dissolution of the specimen, inclusions were separated by centrifuging to avoid contamination of the residue with paper fibers. The samples were carefully washed, the final wash water was removed by means of a pipette, and the centrifuge vials were placed in an oven at  $150^{\circ}\text{C}$  to remove any remaining water.

Extractive methods were chosen from a number of available methods, both chemical and electrolytic. Six methods, two chemical and four electrolytic, were tried.

### 1. Chemical Methods.

#### (a) Iodide - Citrate Method

As suggested by R. J. Bendure<sup>14</sup>, an aqueous iodine-potassium iodide - ammonium citrate solution was tried.



Solutions for this method were made in the following manner:

Iodine - Potassium Iodide

Weigh 240 gr. iodine and 120 gr. potassium iodide.

Add 75 ml. water and digest at low temperature with stirring until dissolved.

Filter through Whatman #42 paper and do not rinse beaker.

Cool and dilute to 200 ml. with water.

Ammonium Citrate - 2%

Weigh 3.16 gr. Citric acid crystals.

Add 1.7 ml. Ammonium hydroxide.

Add 197 ml. Water.

For each 5 grams of sample 50 ml. of the iodine - potassium iodide solution and 25 ml. of the ammonium citrate solution were used. The sample and solutions were placed in a 400 ml. beaker, covered with a proper cover-glass, and left at room temperature for 47 hours and 40 minutes. This was the necessary time required for the dissolution of a 22.7321 gr. sample. The black residue settled to the bottom and was collected for X-ray analysis.



## (b) Bromine - Methanol Method

Mahla and Nielsen<sup>15</sup> were able to isolate carbide particles from stainless steel for electron microscope investigation by the use of a bromine-methanol solution. A solution of 9 ml. bromine and 100 ml. methanol was made and placed over a sample resting in the bottom of a 1000 ml. beaker. This system was kept in a hood at all times to avoid inhalation of bromine fumes. Although sample dissolution occurs by this method, it is extremely slow and after a period of 31 days, very little action had taken place. There were not enough particles remaining to attempt to collect them, so this method was abandoned as being impractical in this case.

## 2. Electrolytic Methods.

All electrolytic methods depended upon the use of the iron sample as the anode and utilized various cathodes and electrolytes. However, in all four methods attempted, the basic electrical circuit was set up according to Fig. 2.



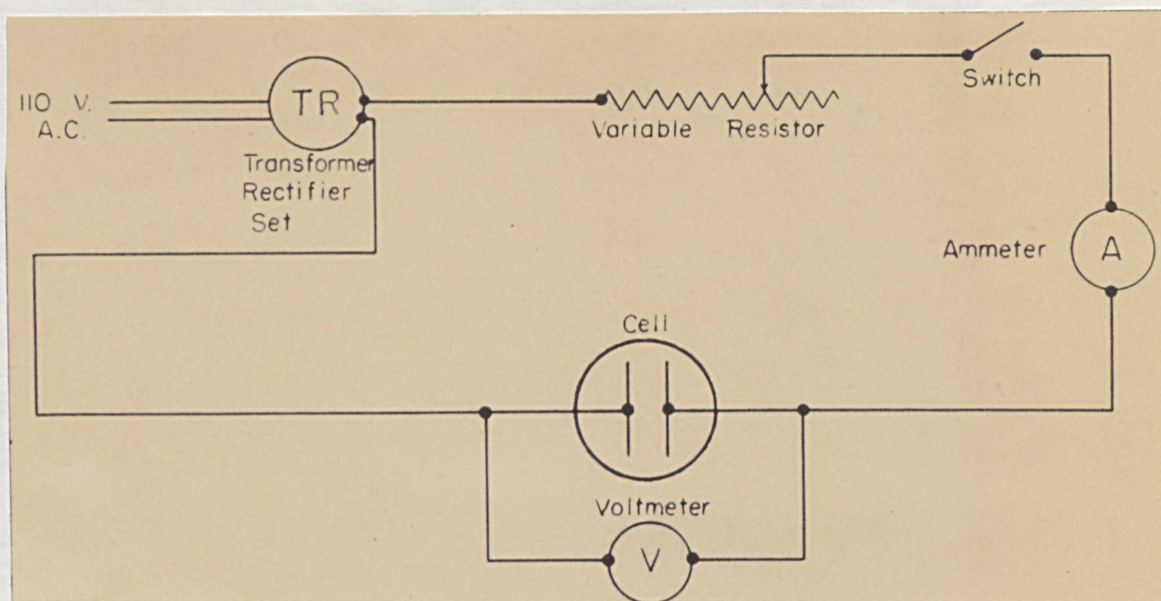


Fig. 2

## BASIC ELECTRICAL CIRCUIT

### (a) Ferric Chloride Method

One possible method of approach to the separation of inclusions is the method of Barnett and Troiano<sup>16</sup> in which the sample is dissolved anodically in a solution consisting of 45 gr. ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in 100 ml. of water. In this method a Monel gauze cathode was used; 0.7 amp. and 1.25 volts were required for the reaction to proceed. To dissolve a sample of 14.6721 grams required a total time of 20 hours and 10 minutes. The brown particles were caught in a canvas sack suspended around the anode.



### (b) Cadmium Bromide Method

In a method for carbide separation described by Scott and Farnham<sup>17</sup>, a cadmium bromide electrolyte was used with good results. It was necessary first in this method to make cadmium bromide from cadmium oxide and hydrobromic acid. These two chemicals were added together and stirred, allowed to cool and crystallize, taken into solution again, and re-cooled to obtain pure cadmium bromide. A solution containing 75 gr. cadmium bromide per 200 ml. water was then made. The sample was suspended vertically as the anode in the electrolytic cell; copper formed the cathode. Cadmium plated out on the cathode at a current of 0.2 amperes. The reddish-brown particles falling off the anode were caught in a canvas sack, reclaimed, and held for X-ray analysis. It required 125 hours and 10 minutes for a 16.5793 gr. sample to dissolve.

### (c) KCl - $\text{HC}_6\text{H}_7\text{O}_7$ Method

It has been reported<sup>18</sup> that an electrolyte consisting of 1N potassium chloride containing 5 gr. citric acid per liter had been used successfully for the isolation of iron carbide. A copper cathode was also used in this system. With a current of 1.0 amp. and a potential of 1.25 volt, a 20.0356 gr. sample was dissolved in 43 hours and



20 minutes. Again the particles were caught in a canvas sack for further investigation. The residue was light-brown.

#### (d) Double Electrolyte Method

The electrolytic cell for this system is shown schematically in Fig. 3. This is a modification of a very successful method of carbide extraction<sup>19</sup>. The anolyte is a solution of 15% sodium citrate, 2% potassium bromide, and 1% potassium iodide; and the catholyte is a 10% copper sulphate solution. A copper cathode is used, and the particles falling from the anode are caught in the porous alundum crucible. A voltage of 1.25 volts and a current of 1.5 amperes was used. For a sample of 24.9879 gr. a total time of 8 hours and 5 minutes was necessary. This is the only method of those attempted that requires careful supervision, because it is essential that fluid flow be from anolyte to catholyte rather than vice versa. To effect this it was necessary to keep the level of the anolyte higher than the level of the catholyte. This was done by the use of a burette suspended above the anode chamber by means of which the anolyte volume could be increased as the electrolyte levels approached one another. The remaining residue was black-brown.



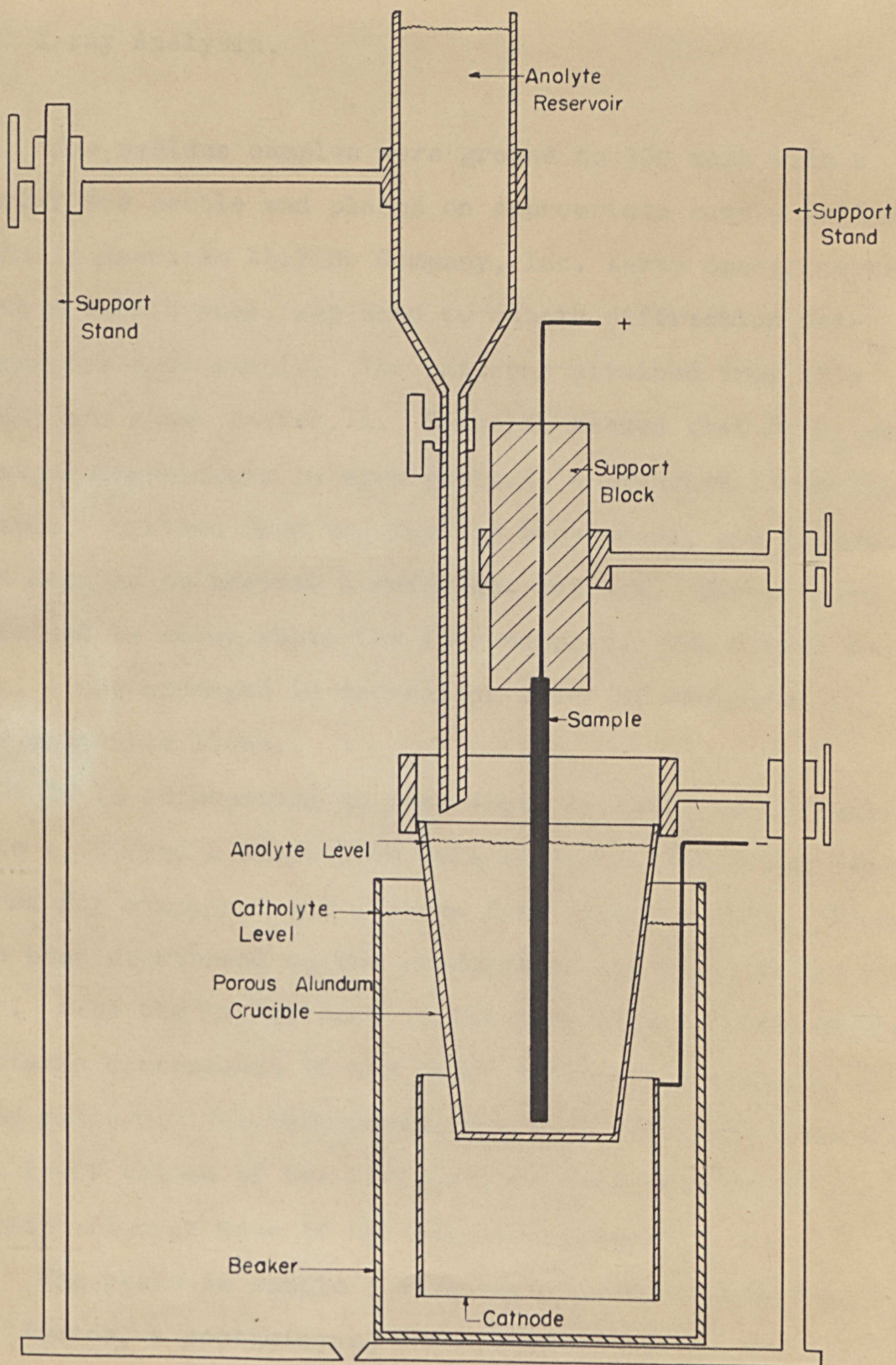


Fig. 3  
SCHEMATIC DIAGRAM - DOUBLE ELECTROLYTE CELL  
 No Scale

E.J.D.



### C. X-ray Analysis.

The residue samples were ground to 300 mesh with a mortar and pestle and placed on appropriate sample holders. A North American Philips Company, Inc. X-ray Spectrometer, with a cobalt tube, was used to obtain diffraction patterns for each sample. The patterns obtained from this study are shown in Fig. 4. Since it seemed that  $\text{Fe}_3\text{O}_4$  was a major constituent in each pattern, a standard magnetite sample, obtained from the Geology Department, was ground and X-rayed to provide a reference pattern. The pattern obtained is shown above the five samples. The charts in Fig. 4 are arranged in decreasing order of sharpness of the magnetite lines.

It is interesting to note that the patterns for samples 1, 5, and 4 slope from left to right, while the patterns for samples 2 and 3 slope from right to left. This has been attributed to the presence of citrates in the former. Also the higher peak at the left side of each of these patterns corresponds to the major peak on the ammonium citrate pattern. The background apparently fluctuates more at the lower values of the diffraction angle because of increased fluorescence of the citrates present.

The peaks in sample 5 have been identified as copper iodide, a contaminant, which apparently was precipitated during the electrolysis and remained associated with the residue.



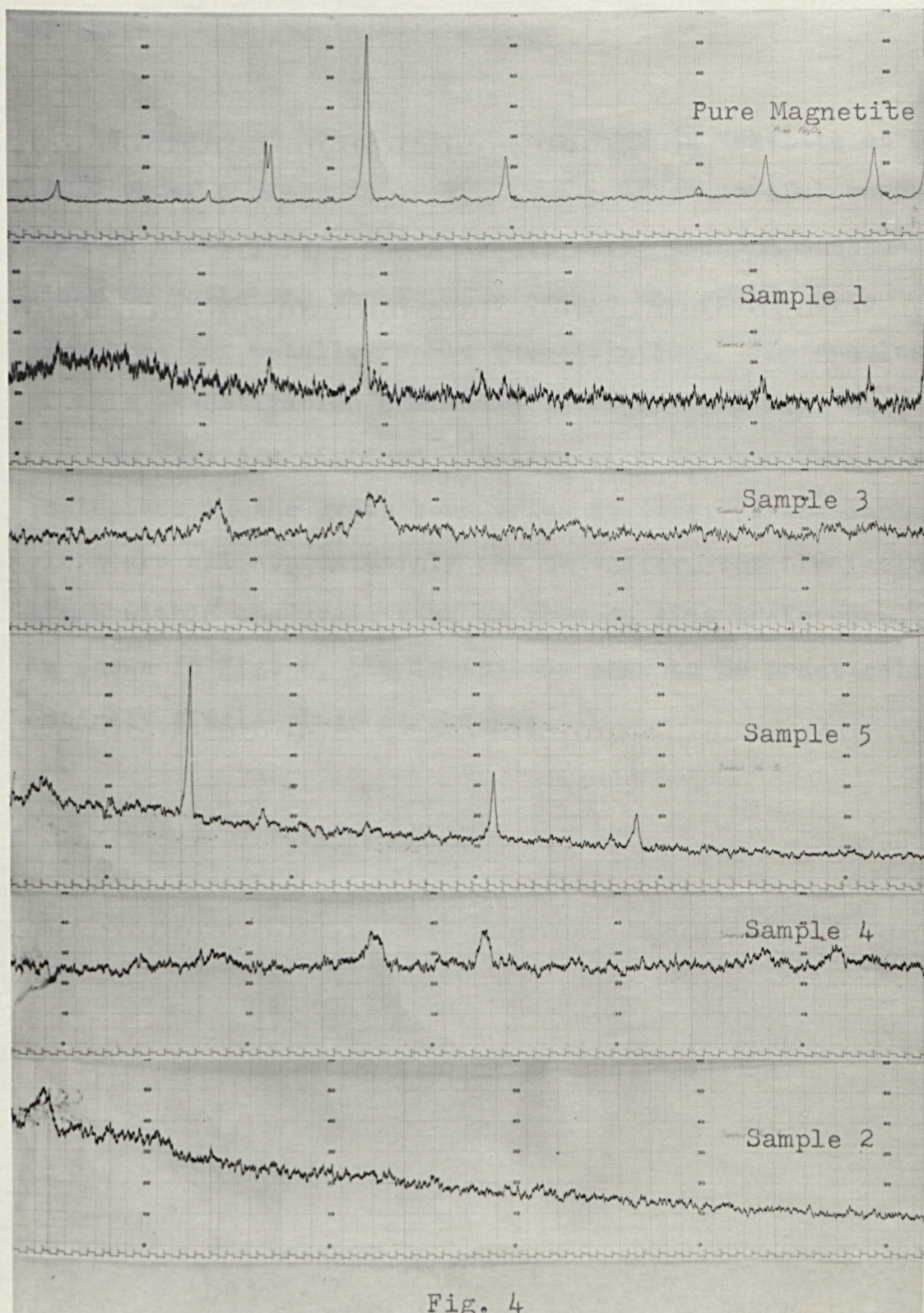


Fig. 4

DIFFRACTION PATTERNS



#### D. Metallographic Investigation.

A sample of Armco iron was mounted in bakelite at 120°C under a pressure of 2000 psi. After careful abrasion on emery papers and polishing with Alundum suspensions on polishing wheels, the sample was etched with 5% picral for metallographic investigation. The results of this investigation are shown in Fig. 5 and Fig. 6.

In Fig. 5 a distinct location of a certain number of inclusions in the grain boundaries is seen. These inclusions are all approximately the same size, but the inclusions within the grain seem to show no size preference. As shown in Fig. 6, the inclusions seem to be practically entirely single-phase structures.



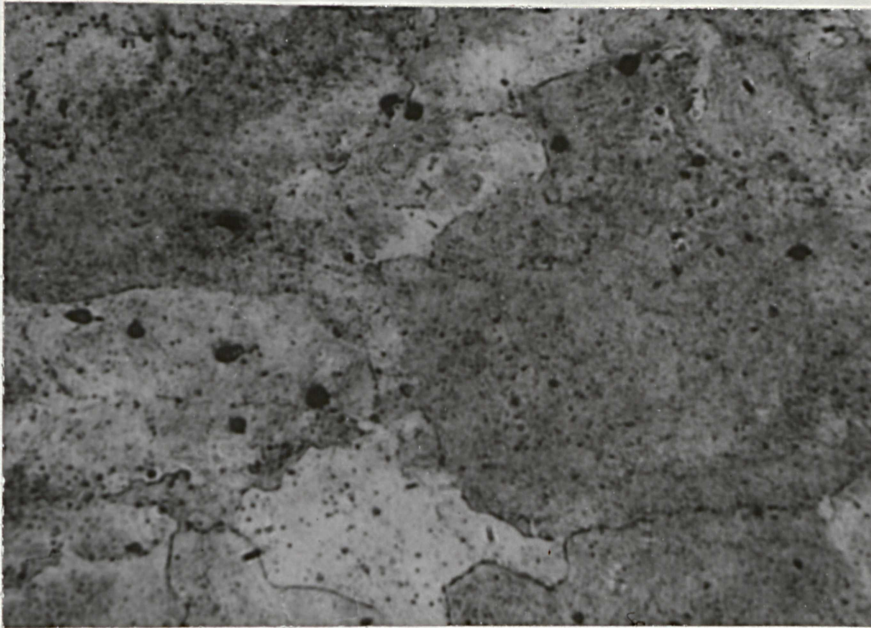


Fig. 5

ARMCO INGOT IRON

5% Picral Etch - 10 sec. 1100x

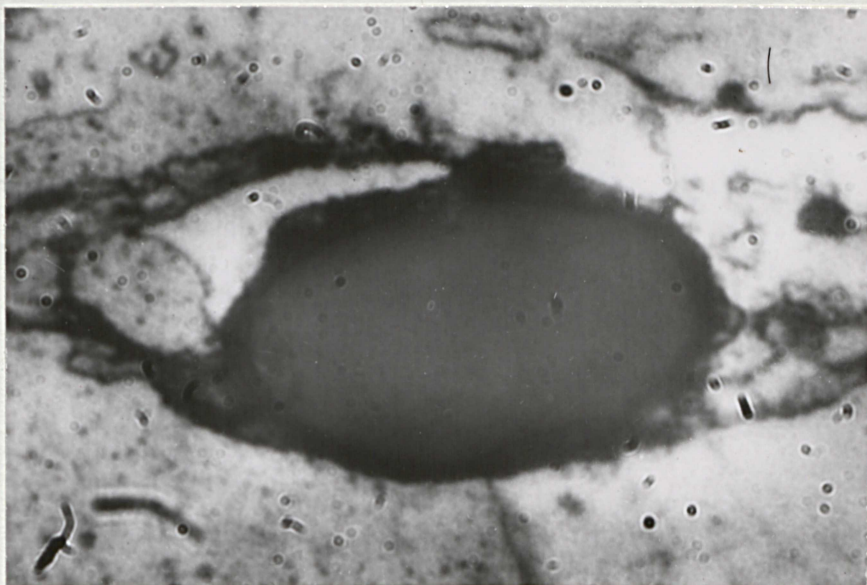


Fig. 6

ARMCO INGOT IRON

5% Picral Etch - 10 sec. 3500x



## APPARATUS

The apparatus for this project is necessarily divided into three sections to correspond with the experimentation.

### Metallographic equipment:

1. Adolph Buehler Company mounting press
2. Standard (0, 00, 000, 0000) emery papers
3. Standard polishing cloths and Alundum suspensions
4. Metallograph

### Separation equipment:

1. Laboratory glassware
2. Variable resistor
3. Weston ammeter
4. Weston voltmeter
5. Rectifier
6. Centrifuge

### X-ray analysis equipment:

1. North American Philips Company, Inc. X-ray Spectrometer (Cobalt Tube)



## EVALUATION OF SEPARATION METHODS

To evaluate the separation techniques, the following tables have been composed.

Table 1

### WEIGHT STUDY OF RESIDUE RECOVERY

Method	Weight of Sample (gr)	Residue Weight (Calc) (gr)	Residue Weight (Actual) (gr)	Residue Color
Iodide-Citrate	22.7321	1.2105	0.8316	Black
Ferric Chloride	14.6721	0.7849	0.5996	Brown
Cadmium Bromide	16.5793	0.8857	0.7279	Red-brown
KCl-HC <sub>6</sub> H <sub>7</sub> O <sub>7</sub>	20.0356	1.0894	0.9436	Lt. brown
Double Electrolyte	24.9879	1.3320	0.8817	Black-brown

Table 2

### TIME STUDY OF RESIDUE RECOVERY

Method	Weight of Sample (gr)	Time Required (hr)	Time per Gram Sample (hr)
Iodide-Citrate	22.7321	47.667	2.095
Ferric Chloride	14.6721	20.167	0.993
Cadmium Bromide	16.5793	125.167	7.558
KCl-HC <sub>6</sub> H <sub>7</sub> O <sub>7</sub>	20.0356	43.333	2.159
Double Electrolyte	24.9879	8.083	0.324



In an evaluation of the best technique, the several points shown above in the tables must be considered. First, the color of the residue is important. If magnetite is assumed, as a result of the X-ray patterns, to be the most prominent constituent, then the color of the residue should be black. In only one case is this true; in each of the other techniques, which are all electrolytic, the color varies. This may be due to one or both of two possible phenomena:

1. If  $\text{Fe}_3\text{O}_4$  is the major particle, further oxidation and conversion to  $\text{Fe}_2\text{O}_3$  is possible in the electrolyte itself.

2.  $\text{Fe}(\text{OH})_3$  or other hydroxides may form during electrolysis or chemical dissolution of the iron and remain with the residue.

From the X-ray patterns,  $\text{Fe}_3\text{O}_4$  peaks in all but sample 1 are not sharp, but instead are spread over a wider area. This would seem to indicate the presence of very fine or partially decomposed  $\text{Fe}_3\text{O}_4$  in all except the residues from sample 1. If the second statement were completely true, both  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}(\text{OH})_3$  or some other hydroxide lines should appear. This does not seem to be the case. Therefore, some decomposition of  $\text{Fe}_3\text{O}_4$  in the corroding solution seems to be occurring.

Secondary factors to be considered are the time required and the weight of the recovered residue. The Double Electrolyte Method is the most time efficient, but



this fact must be balanced with the close supervision necessary in this method. Judging from the X-ray pattern the Ferric Chloride Method does not seem to give anticipated results, even though it is more time efficient. The weights of calculated residue and actual residue should not be used as a measure of efficiency of the methods. The rather limited nature of the lineal analysis performed, the possible losses of sample incurred in handling, and the assumption of a constant specific density of the inclusions make the weight factor a somewhat questionable criterion.

Consideration of these points plus the generally more satisfactory X-ray pattern, indicates that the Iodide-Citrate Method is the best to use for oxide extraction in Armco iron. The residue color is correct, assuming again that magnetite is prevalent; the residue is magnetic; and the method is fairly rapid, the speed of extraction might possibly be increased by change in temperature of the system. It should be pointed out, however, that the solution preparation for this method is much more time consuming than was the case for the other solutions investigated.



## DISCUSSION AND CONCLUSIONS

From the results attained in this work, it seems that the Iodide-Citrate Method is the most satisfactory for separation of inclusions from Armco ingot iron. These inclusions apparently are chemically reacted upon, or otherwise contaminated, or both, during electrolysis or chemical dissolution of the iron in the other baths which were selected for this work. It cannot be definitely stated that the Iodide-Citrate Solution Mixture provides the optimum method of separation, because a limited number of solutions were investigated in this work. It can only be stated that of the methods tried this one seemed to give the best results. Reasons for this conclusion are based both on the appearance of the residue and more especially on the sharpness of the lines in the X-ray diffraction pattern. A point of interest here is the emphatic indication of the need for care and precautions in analyzing X-ray data and in the selection of the initial solutions. The presence of contaminants in the residue is a likely possibility, and their presence makes analysis of X-ray data more difficult and less positive.

Metallographically, it is possible to see a rather distinct preferential location of a certain amount of inclusions at the grain boundaries. Generally, these are practically all approximately the same size. On the other



hand, the larger portion of the inclusions is found distributed at random throughout the grains, and seems to show no particular size preference. They do seem to reach a limit in maximum size, and from this maximum decrease in size so that the finest are almost indistinguishable at the highest magnification attainable with a light microscope.

With regard to shape, the inclusions (particularly inside the grains) are roughly circular in cross section and therefore, apparently solidify as spheroids in the iron matrix. None were observed which showed any particular geometric shape, and it seems logical to conclude that the solidification of the iron occurred in advance of the solidification of the inclusion material. This lag in solidification of inclusions, after that of the iron is complete, means that after the iron has become solidified, at least the large proportion of the inclusions is still in the molten state, hence, their assumption of a spherical shape.

The inclusions themselves seem to be practically entirely single-phase structures with no evidence of second or third phases around their peripheries as might be expected if a reaction occurred at the surface of the inclusions. On the basis of magnetic behavior of the extracted residue and the fairly conclusive evidence for magnetite in the X-ray pattern, the author is led to believe that the single phase shown is  $\text{Fe}_3\text{O}_4$ . Since this



compound is inherently ferro-magnetic, possibly the peculiar ferro-magnetic behavior of Armco iron as reported by Arthur P. Woods, Jr.<sup>20</sup> might well be expected.



## SUGGESTIONS FOR FURTHER INVESTIGATION

1. Further studies might be made concerning the composition of all the inclusions, both in the grain boundaries and within the grains themselves. A difference in composition between these two might be noticed.
2. Study additional solvents, both chemical and electrolytic.
3. The effect of different conditions might be studied to determine the optimum extraction conditions.



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